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Free volume distribution of branched poly(methyl methacrylates): Conformational probes study

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ABSTRACT

In this work we studied the free volume distribution of the branched poly (methylmethacrylates) by the method of conformational probes. The freezing temperatures of the conformational transitions of the probes introduced into branched polymers were determined by FTIR spectra. The influence of covalently connected fullerene C_{60} on the freezing temperatures of conformational transitions was shown.

1. Introduction

Local conformational dynamics of macromolecules and free volume distribution determine many physical properties of linear and branched polymers. Branched polymers are characterized by high solubility in various organic media, low viscosity of solutions and melts compared to linear polymers of the same molecular structure, high sorption and low-molecular compound transport. These properties of branched polymers are due to the topological structure that is characterized by a high concentration of end chains and branching junctions in the peripheral layer and in the core of a macromolecule [1]. The branched polymers are of great interest for their application as pharmacological nanocontainers in medicine and nanocontainers of functional additives in mass production of modified polymers [2–5].

In studying the possibilities of use of branched polymers, we need information on local molecular mobility, free volume distribution and transport of low-molecular compounds in branched polymers as in case of linear ones. For that, we use the method of conformational probes [6] based on investigating conformational behavior of a low-molecular-weight compound introduced as a probe into an amorphous glassy polymer. The value of the equilibrium constant K is determined by the expression:

$$K = \exp(-\Delta H_0/RT + \Delta S_0/R),$$

where ΔH_0 and ΔS_0 are the enthalpy and entropy differences of the conformers. A decrease of the temperature causes a redistribution of conformer's concentrations, i.e. a shift of conformational equilibria. Consequently, the intensities of conformer infrared absorption bands are redistributed. According to the Beer's law, the integrated intensities I_t and I_g of the absorption bands of the *trans* and *gauche* conformers are defined by:

$$\ln(I_t/I_g) = \ln(\alpha_t/\alpha_g) - \Delta H_0/RT + \Delta S_0/R = \ln K + \ln(\alpha_t/\alpha_g),$$

where α_t and α_g are the integral absorption coefficients of the utilized bands. If there are conformational transitions in the system and $\Delta H_0 \neq 0$ then the experimental value $ln(I_t/I_g)$ must depend on the temperature. If at a certain temperature T_f the conformational transitions freeze, it is definitely due to a particular process taking part in the polymer. The conformational probe is characterized by the activation volume $V_p^{\neq}$, i.e. the minimum volume required for the conformational transition to occur. Since at $T < T_f$ the conformational transitions of the probe molecules do not occur, we may conclude that at these temperatures the effective maximum size of free volume elements is smaller than $V_p^{\neq}$. The transition of the molecule from one conformation into another may occur when the effective maximum volume is close to or larger than $V_p^{\neq}$. Comparing the structure of the probe and the polymer, one may determine the type of secondary relaxation transitions and the free

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